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Concept for long-term biomonitoring of residues from plant protection products within the monitoring measure of the Swiss Action Plan on plant protection products

WP1: Substance selection for Soil Guideline Value (SGV) derivation – selection criteria and procedure

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External Report

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Summary

As part of the concept proposal for the long-term biomonitoring of residues from plant protection products within the monitoring measure of the Swiss Action Plan on plant protection products, work package 1 (WP1) includes, as a first step, the selection of ten substances of interest for the subsequent derivation of Soil Guideline Values (SGVs). Ten substance dossiers will be compiled accordingly for these selected substances.

The ten first selected candidates were chosen from the list of 144 substances established by the NABO (state November 2019) regarding the monitoring of PPP residues in agricultural soils. The criteria taken into consideration and included in a stepwise procedure for selecting the ten substances were the following: the substance "mean score" (according to the NABO substance list), if the substance was still authorized for use in Switzerland (state March 2020) as well as the PPP category (i.e. fungicide, herbicide, insecticide/acaricide). For substances showing equal mean score, additional criteria such as the volume of substance sold per year, the persistency of the substance in the soil or the highest "ecotoxicology score"[1] (i.e. ecotox score of 1 according to the NABO substance list) were used for the selection process.

Two additional substances (i.e. s-metolachlor and pirimicarb), included in the NABO list on expert recommendations after the 3rd workshop, were also taken into consideration, resulting in a selection of twelve substances. After expert consultation, the first selection was revised and a final selection was made. A total of ten dossiers and derived SGV will be provided for the following substances (see also Figure 2):

- *Fungicides*: **difenoconazole, fluazinam, azoxystrobin, tebuconazole**
- *Herbicides*: **oryzalin, pendimethalin, s-metolachlor**
- *Insecticides/acaricides*: **fenpyroximate, tebufenozide, pirimicarb**

Moreover, it was verified that these substances were candidates for the NABO PPPs multiresidue analysis, i.e. they were given a score of 1 (= max. weighting for analysis potential) for this criterion in the NABO substance list. The different steps of the selection procedure are described below.

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[1]Among substances on the NABO list, substances with an ecotox score of 1 (maximum score, with scores ranging from 0 to 1) reflect compounds with the highest toxicity potential for soil organisms, i.e. the ones that in point of view of their individual toxicity and their bioaccumulation potential could be the most problematic for soil organisms.

Content

Selection procedure

1.1 Identification of NABO "Top 24" substances according to mean score

The 144 substances listed by NABO were ranked in descending order according to their mean score. The mean score, which is taking into account the "application", "environmental behavior" and "ecotoxicology" scores (see Figure 1 below and NABO report "AP PSM Massnahme 6.3.3.7 Bodenmonitoring Jahresbericht 2019" for more details), reflects the relevance of the substance for the monitoring: the higher the score, the more relevant the substance is for the monitoring of PPP residues in soils.
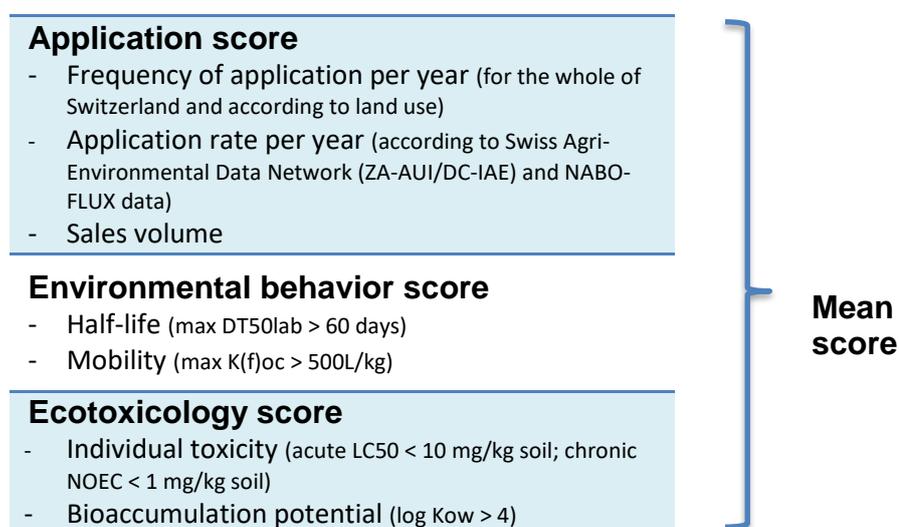

Application score
- Frequency of application per year (for the whole of Switzerland and according to land use)
- Application rate per year (according to Swiss Agri-Environmental Data Network (ZA-AUI/DC-IAE) and NABO-FLUX data)
- Sales volume

Environmental behavior score
- Half-life (max DT50lab > 60 days)
- Mobility (max K(f)oc > 500L/kg)

Ecotoxicology score
- Individual toxicity (acute LC50 < 10 mg/kg soil; chronic NOEC < 1 mg/kg soil)
- Bioaccumulation potential (log Kow > 4)

Mean score

Figure 1: Scoring categories and associated criteria composing the mean score of the NABO list of 144 substances (according to NABO excel file "Substanzauswahl Mögliche Kandidaten für AP PSM6337").

In order to select ten candidates for SGV derivation, substances were ranked in descending order according to their mean score. The top five substances were selected, which had a mean score between 0.92 and 0.72, with scores ranging from 0 (minimum score) to 1 (maximum score). Since the following nineteen substances all had a mean score of 0.69, no further selection according to the mean score could be conducted. These nineteen substances plus the top five substances were selected in the first step of the selection procedure resulting in twenty-four substances (Table 1). The remaining substances on the NABO list, with a score of 0.67 and below, were not considered further.

Table 1: First step of the selection procedure: "top 24" of the 144 substances on the NABO list, ranked according to the highest mean score.

Substance	Application score	Env. behavior score	Ecotox score	Mean score
Difenoconazole	0.75	1	1	0.917
Oryzalin	0.75	1	1	0.917
Fluazinam	0.42	1	1	0.806
Azoxystrobin	0.75	1	0.5	0.75
Pendimethalin	0.67	1	0.5	0.722
Aclonifen	0.58	1	0.5	0.694
Chlorphacinon	0.08	1	1	0.694
Chlorpyrifos	0.08	1	1	0.694
Clomazone	0.08	1	1	0.694
Cyproconazole	0.08	1	1	0.694
Difenacoum	0.08	1	1	0.694
Diuron	0.58	1	0.5	0.694
Fenazaquin	0.08	1	1	0.694
Fenpyroximate	0.08	1	1	0.694
Fipronil	0.08	1	1	0.694
Flocoumafen	0.08	1	1	0.694
Forchlorfenuron	0.08	1	1	0.694
Metconazole	0.08	1	1	0.694
Paclobutrazol	0.08	1	1	0.694
Picolinafen	0.08	1	1	0.694
Propiconazole	0.08	1	1	0.694
Pyraclostrobin	0.08	1	1	0.694
Tebuconazole	0.08	1	1	0.694
Teflubenzuron	0.08	1	1	0.694

1.2 Authorization for use in Switzerland

As a next step, it was verified that the twenty-four pre-selected substances were still authorized for use in Switzerland (state March 2020; source: SR 916.161 Pflanzenschutzmittelverordnung, PSMV: Anhang 1: Für die Verwendung in Pflanzenschutzmitteln genehmigte Wirkstoffe / RS 916.161 Ordonnance sur la mise en circulation des produits phytosanitairs, OPPh: Annexe 1: Substances actives approuvées dont l'incorporation est autorisée dans les produits phytosanitaires, as well as the Pflanzenschutzmittelverzeichnis BLW / Index des Produits Phytosanitaires, OFAG). Eight substances, i.e. chlorphacinon, difenacoum, fenazaquin, fipronil, flocoumafen, forchlofenuron, picolinafen and teflubenzuron, are no longer approved in Switzerland and were removed from the list. It was considered that for these unauthorized substances, no further actions can be taken to reduce the risk of PPP residues under the national Action Plan. Furthermore, the risk for soil organisms should decrease over time if these substances are no longer applied. Sixteen substances were remaining in the pre-selection (Table 2).

Table 2: Second step of the selection procedure: removal of substances with unauthorized use in Switzerland (state March 2020; source: Annexe 1 of the OPPh, RS 916.161 and "Index des Produits Phytosanitaires", OFAG/BLW) resulted in sixteen remaining substances (f: fungicides, h: herbicides, i/a: insecticides/acaricides).

Substance	Application score	Env. Behavior score	Ecotox score	Mean score	PPP Categories
Difenoconazole	0.75	1	1	0.917	f
Oryzalin	0.75	1	1	0.917	h
Fluazinam	0.42	1	1	0.806	f
Azoxystrobin	0.75	1	0.5	0.75	f
Pendimethalin	0.67	1	0.5	0.722	h
Chlorpyrifos	0.08	1	1	0.694	i/a
Clomazone	0.08	1	1	0.694	h
Cyproconazole	0.08	1	1	0.694	f
Fenpyroximate	0.08	1	1	0.694	i/a
Metconazole	0.08	1	1	0.694	f
Paclobutrazol	0.08	1	1	0.694	f
Propiconazole	0.08	1	1	0.694	f
Pyraclostrobin	0.08	1	1	0.694	f
Tebuconazole	0.08	1	1	0.694	f
Aclonifen	0.58	1	0.5	0.694	h
Diuron	0.58	1	0.5	0.694	h

1.3 PPP categories

As a fourth step, in order to ensure a good representativeness of the different PPP categories (i.e. fungicide, herbicide, insecticide/acaricide) within the chosen substances, a selection from the list of sixteen remaining substances was made accordingly. As far as possible, a balanced number of substances from the fungicide, herbicide or insecticide/acaricide category were chosen. Moreover, substances with the highest mean score were preferred.

1.3.1 Fungicides

Nine fungicides were present among the sixteen remaining substances of the selection procedure (Table 3). Difenoconazole and fluazinam, ranked at the top of the list with a mean score of 0.92 and 0.81, respectively, were included in the candidate list for SGV derivation. Azoxystrobin with the third highest mean score of 0.75 was also selected. Finally, from the six remaining fungicidal candidates, tebuconazole was chosen. Although all six fungicides had a mean score of 0.69, tebuconazole was the most widely sold with a volume of 3.768 tons in 2018 (source: BLW/OFAG).

1.3.2 Herbicides

Among the sixteen remaining substances, five of them were herbicides (Table 3). The two first herbicides on the list, oryzalin (mean score of 0.92) and pendimethalin (mean score of 0.72) were included in the candidate list. Among the three remaining herbicide candidates (i.e. clomazone, aclonifen and diuron), all with a mean score of 0.69, clomazone was selected first as it has the highest ecotox score (ecotox score of 1). Between aclonifen and diuron, the preference was given to diuron rather than aclonifen due to its highest sales volume (4.78 tons in 2018) and its persistence in soil. Indeed, a DT50 in soil of 4 to 8 months is reported for diuron, whereas for aclonifen the DT50 in soil is 36 to 80 days at 22°C (Tomlin 2009).

1.3.3 Insecticides/acaricides

Only two insecticides/acaricides were present among the sixteen remaining substances of the pre-selection (Table 3). Chlorpyrifos and fenpyroximate were thus integrated it the candidate list for SGV derivation.

Table 3: Third step of the selection procedure: selection according to PPP categories; selected fungicides (in orange), herbicides (in yellow) and insecticides/acaricides (in blue) to be included in the substance list for SGV derivation (f: fungicides, h: herbicides, i/a: insecticides/acaricides).

Substance	Application score	Env. behavior score	Ecotox score	Mean score	PPP Categories
Difenoconazole	0.75	1	1	0.917	f
Oryzalin	0.75	1	1	0.917	h
Fluazinam	0.42	1	1	0.806	f
Azoxystrobin	0.75	1	0.5	0.75	f
Pendimethalin	0.67	1	0.5	0.722	h
Chlorpyrifos	0.08	1	1	0.694	i/a
Clomazone	0.08	1	1	0.694	h
Cyproconazole	0.08	1	1	0.694	f
Fenpyroximate	0.08	1	1	0.694	i/a
Metconazole	0.08	1	1	0.694	f
Paclobutrazol	0.08	1	1	0.694	f
Propiconazole	0.08	1	1	0.694	f
Pyraclostrobin	0.08	1	1	0.694	f
Tebuconazole	0.08	1	1	0.694	f
Aclonifen	0.58	1	0.5	0.694	h
Diuron	0.58	1	0.5	0.694	h

1.4 Additional candidates

Two additional substances, the insecticide pirimicarb and the herbicide s-metholachlor, were added to the substance list for SGV derivation (Table 4). Together with the herbicide atrazine, these three substances were added on the NABO substance list following expert recommendations during the workshop held in September 2019. These substances have generated some controversy, as for example, metabolites of s-metholachlor have been frequently found in Swiss groundwaters in recent years (BAFU 2019). With 22.423 tons per year, this herbicide was also among one of the most sold active substances in Switzerland in 2018. Pirimicarb belongs to the family of carbamate and therefore represents a different mode of action compared to the two other selected insecticides/acaricides (chlorpyrifos and fenpyroximate). It is also a substitute candidate listed in the attachment 9.1 of the Swiss Action Plan. Since atrazine is not authorized for use in Switzerland anymore, it was not considered for SGV derivation.

Table 4: Fourth step of the selection process: substances added on the NABO list, on expert recommendations after the AP PSM Workshop in September 2019.

Substance	Application score	Env. behavior score	Ecotox score	Mean score	Reason for selection
Pirimicarb	0.42	1	0	0.472	Expert decision
S-Metolachlor	0.67	0	0.5	0.389	Expert decision
Atrazine	Not evaluated				Expert decision

2 First selection

Twelve substances were finally selected as candidates for a SGV derivation attempt. Among these were four fungicides, five herbicides and three insecticides/acaricides (Table 5). After a preliminary search and check for the availability of soil ecotox data for these active substances, mainly in EU (re-)authorization dossiers and Pesticides Properties DataBase (PPDB), seven substances (i.e. difenoconazole, oryzalin, fluazinam, chlorpyrifos, clomazone, tebuconazole, s-metolachlor) showed to likely have sufficient soil ecotox data for a SGV derivation. We therefore suggest to continue with a dossier development and SGV derivation for these seven active substances by retrieving additional data from the literature (see also Table 5).

For the five other substances (i.e. fenpyroximate, azoxystrobin, pendimethalin, diuron, pirimicarb), soil ecotox data are very limited in EU (re-)authorization dossiers and PPDB. A SGV dossier will be elaborated only for the three out of the five substances that will present the most reliable and relevant ecotox data from the literature. In the end, a total of ten substance dossiers and derived SGV will be developed.

Table 5: Final substance selection for the final ten SGV dossiers. The seven substances colored in black are suggested to be taken for SGV derivation. For substances colored in red, only three out of the five will be retained for SGV derivation, based on the amount and quality of the ecotox data retrieved from the literature (f: fungicides, h: herbicides, i/a: insecticides/acaricides).

Substance	Application score	Env. behavior score	Ecotox score	Mean score	Reason for selection	PPP Categories
Difenoconazole	0.75	1	1	0.917	Score	f
Oryzalin	0.75	1	1	0.917	Score	h
Fluazinam	0.42	1	1	0.806	Score	f
Azoxystrobin	0.75	1	0.5	0.75	Score	f
Pendimethalin	0.67	1	0.5	0.722	Score	h
Chlorpyrifos	0.08	1	1	0.694	Score	i/a
Clomazone	0.08	1	1	0.694	Score	h
Fenpyroximate	0.08	1	1	0.694	Score	i/a
Tebuconazole	0.08	1	1	0.694	Score	f
Diuron	0.58	1	0.5	0.694	Score	h
Pirimicarb	0.42	1	0	0.472	Expert decision	i/a
S-Metolachlor	0.67	0	0.5	0.389	Expert decision	h

3 Final selection after consultation

After this first list of candidate substances was compiled, this report was sent out in May 2020 to all the attendees of the 3rd PPP-Monitoring workshop in September 2019 for feedback on the substance selection. Out of 24 people, we received feedback from two persons pointing out that chlorpyrifos and diuron are currently under re-evaluation for authorization in Switzerland and will presumably not be allowed anymore for usage and application in Switzerland. This information was not evident from the sources we consulted to check the authorization status for substances used in PPP in Switzerland at this point of time (see chapter "Authorization for use in Switzerland", p.4), but was confirmed with the FOAG. We therefore decided to replace chlorpyrifos and diuron with other substances from the NABO substance list. We reduced the list of twelve to a list of ten candidate substances while intending to have a balanced number of substances in each category. The four fungicides difenoconazole, fluazinam, azoxystrobin and tebuconazole remained candidate substances. Out of the five herbicide candidates and beside the elimination of diuron for the reason explained above, we also decided to eliminate clomazone from the candidate list as it presented a low mean score combined with a low sales volume in regard to the other herbicides. Hence, three candidate herbicides remained: oryzalin, pendimethalin and s-metolachlor. Finally, chlorpyrifos was replaced by the insecticide tebufenozide, leaving three insecticides/acaricides on the list: fenpyroximate, tebufenozide and pirimicarb. Tebufenozide was selected as replacement, since it had a high sales amount (674 kg) in 2019. Even though not classified as persistent in the registration dossiers, according to the Pesticide Properties DataBase (PPDB), tebufenozide is rated very persistent by Arvalis, the French arable crops R&D institute and is therefore an interesting candidate substance.

Table 6: Final substance selection for the final ten SGV dossiers after expert consultation (f: fungicides, h: herbicides, i/a: insecticides/acaricides).

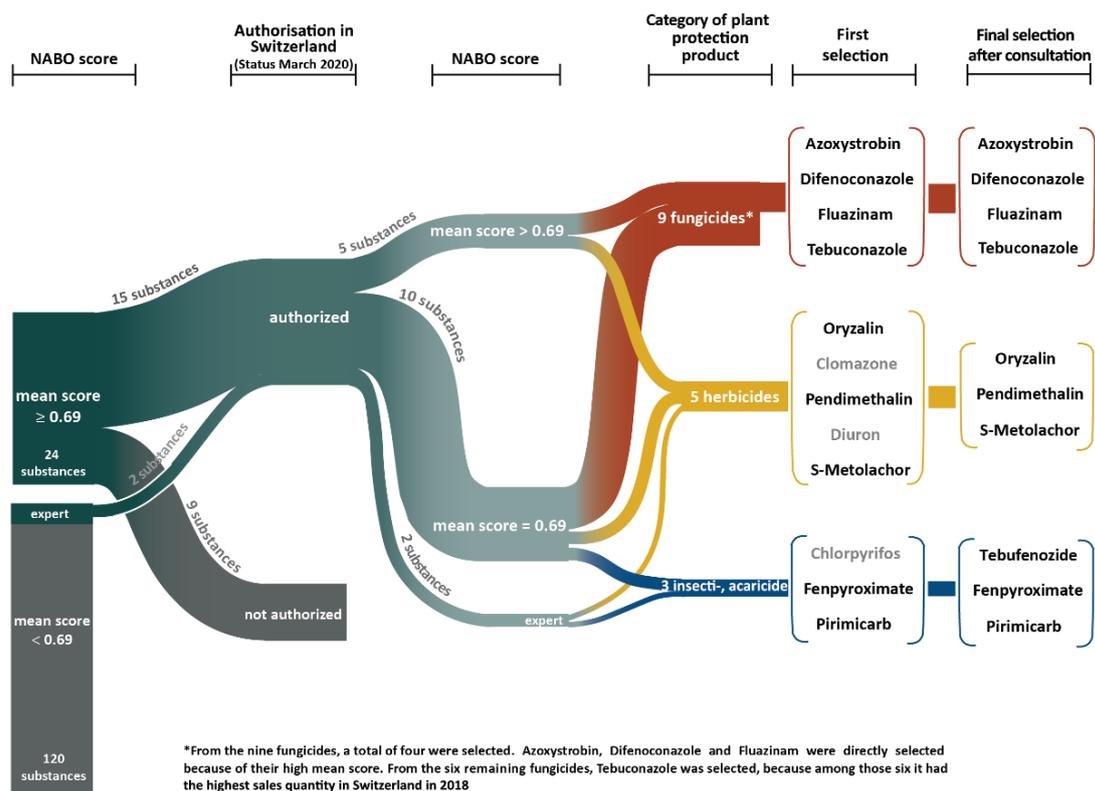| Substance	Application score	Env. behavior score	Ecotox score	Mean score	Reason for selection	PPP Categories
Difenoconazole	0.75	1	1	0.917	Score	f
Oryzalin	0.75	1	1	0.917	Score	h
Fluazinam	0.42	1	1	0.806	Score	f
Azoxystrobin	0.75	1	0.5	0.75	Score	f
Pendimethalin	0.67	1	0.5	0.722	Score	h
Fenpyroximate	0.08	1	1	0.694	Score	i/a
Tebuconazole	0.08	1	1	0.694	Score	f
Tebufenozide	0.08	1	0.5	0.528	Score	i/a
Pirimicarb	0.42	1	0	0.472	Expert decision	i/a
S-Metolachlor	0.67	0	0.5	0.389	Expert decision	h

Figure 2: Stepwise procedure for substance selection for SGV derivation. Substances in grey were eliminated or replaced by another substance of the first selection after expert consultation.

4 Outlook

Parallel to the ongoing search and evaluation of ecotoxicolocial data for SGV derivation, we are currently summarizing the different international methodologies that other countries use for the derivation of soil protection values in a literature review. This review aims at summarizing the main approaches currently available and at highlighting the differences amongst the existing methods and applications. This will provide the basis for the experts and stakeholders to take decisions about the appropriate methodology and applicability of deriving soil protection values in Switzerland. In order to facilitate the selection of the appropriate methodology, we are also compiling case studies with two substances where we compare certain methodologies. The case studies will help to identify advantages and disadvantages of the different international methodologies. Once the methodology will be selected for Switzerland, the respective dossiers for the ten selected substances will be compiled and the corresponding SGV will be derived. Since dossier development for one single substance takes eight to ten weeks, the time and resources available for additional substances is limited within WP1.

5   References

BAFU (Hrsg.) 2019: Zustand und Entwicklung Grundwasser Schweiz. Ergebnisse der Nationalen Grundwasserbeobachtung NAQUA, Stand 2016. Bundesamt für Umwelt, Bern. Umwelt-Zustand Nr. 1901: 138 S / OFEV (éd.) 2019: État et évolution des eaux souterraines en Suisse. Résultats de l'Observation nationale des eaux souterraines NAQUA, état 2016. Office fédéral de l'environnement, Berne. État de l'environnement no1901: 144p

Nationale Bodenbeobachtung (NABO) 2019, AP PSM Massnahme 6.3.3.7 Bodenmonitoring, Jahresbericht 2019

Pflanzenschutzmittelverzeichnis BLW / Index des Produits Phytosanitaires, OFAG:

SR 916.161 Pflanzenschutzmittelverordnung, PSMV: Anhang 1: Für die Verwendung in Pflanzenschutzmitteln genehmigte Wirkstoffe / RS 916.161 Ordonnance sur la mise en circulation des produits phytosanitairs, OPPh: Annexe 1: Substances actives approuvées dont l'incorporation est autorisée dans les produits phytosanitaires

Tomlin, C D S. 2009. The Pesticide Manual. 15th Editi. Alton, UK: British Crop Production Council (BCPC).